

Graphene Nanoribbon and Graphene Nanodisk

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Abstract

We study electronic properties of graphene derivatives which have closed edges. They are finite-length graphene nanoribbons and graphene nanodisks. No metallic states are found in finite-length zigzag nanoribbons though all infinite-length zigzag nanoribbons are metallic. We also study hexagonal, parallelogrammic and trigonal nanodisks with zigzag or armchair edges. No metallic states are found in these nanodisks either except trigonal zigzag nanodisks. It is interesting that we can design the degeneracy of the metallic states arbitrarily in trigonal zigzag nanodisks by changing the size.

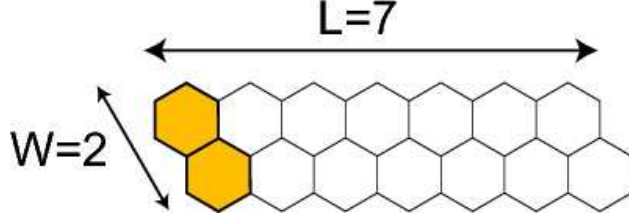


FIG. 1: (Color online) Geometric configuration of zigzag graphene nanoribbons with width W and length L . Here we show the example of the $(W, L) = (2, 7)$ nanoribbon. The basic chain is W connected benzene depicted in orange (gray).

Introduction: Graphene based nanostructure may be an alternative to silicon based mesostructure in future electronic devices. Among them graphene nanoribbons^{1,2,3,4,5,6} have attracted much attention due to a rich variety of band gaps, from metals to wide-gap semiconductors. It is intriguing that all zigzag nanoribbons have zero-energy states^{1,2} and hence they are metallic.

In order to make nanoelectronic circuits, however, nanoribbons must have finite length. It is important to investigate the finite-length effects on the electronic properties of nanoribbons. In this paper, we study whether finite-length zigzag nanoribbons have zero-energy states to know if they are metallic or not.

Graphene has a two-dimensional structure, while a graphene nanoribbon has a one-dimensional structure. We may likewise consider a zero-dimensional structure, that is, a graphene nanodisk. A graphene nanodisk is a nanometer-scale disk-like material characterized by a discrete energy spectrum. Some of nanodisks have already been manufactured by soft-landing mass spectrometry⁷. In this paper, we also study the electric properties of typical nanodisks in quest of zero-energy states. A combination of nanoribbons, nanodisks and other graphene derivatives is a promising candidate of nanoelectronic circuits⁸.

Finite-length graphene nanoribbons: A classification of infinite-length nanoribbons is given in a previous work². In this paper we concentrate on finite-length zigzag nanoribbons. We classify them as follows (Fig.1). First we take a basic chain of W connected carbon hexagons, as depicted in orange (dark gray). Second we translate this chain. Repeating this translation L times we construct a nanoribbon indexed by a set of two integers (W, L) . In what follows we analyze a class of finite-length nanoribbons generated in this

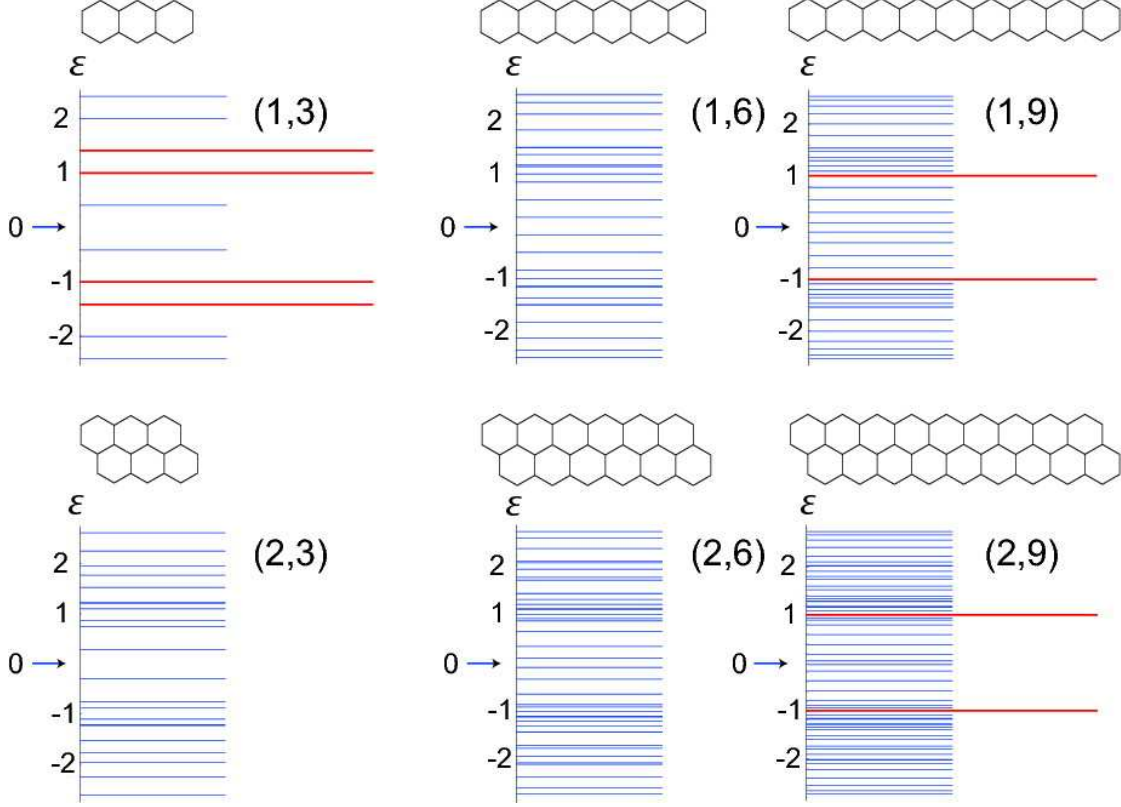


FIG. 2: (Color online) Density of states of finite-length nanoribbons. The vertical axes is the energy ε in units of $t = 3\text{eV}$ and the horizontal axes is the degeneracy. There exist no zero-energy states.

way. Parameters W and L specify the width and the length of nanoribbons, respectively. The infinite-length nanoribbons are obtained by letting $L \rightarrow \infty$.

Energy spectrum: We calculate the energy spectrum based on the nearest-neighbor tight-binding model, which has been successfully applied to the studies of carbon nanotubes and nanoribbons. The Hamiltonian is defined by

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j, \quad (1)$$

where ε_i is the site energy, t_{ij} is the transfer energy, and c_i^\dagger is the creation operator of the π electron at the site i . The summation is taken over all nearest neighboring sites $\langle i, j \rangle$. Owing to their homogeneous geometrical configuration, we may take constant values for these energies, $\varepsilon_i = \varepsilon_F$ and $t_{ij} = t$. Then, the diagonal term yields just a constant, $\varepsilon_F N_C$, and can be neglected in the Hamiltonian (1), where N_C is the number of carbon atoms in

a nanoribbon or nanodisk. This is because there exists one electron per one carbon: The band-filling factor is $1/2$.

We diagonalize the Hamiltonian (1) explicitly to derive the density of states for finite-length nanoribbons. It can be shown that the determinant associated with the Hamiltonian (1) has a factor such that

$$\det [\varepsilon I - H(N_C)] \propto (\varepsilon - t)^{a(W,L)} (\varepsilon + t)^{a(W,L)}, \quad (2)$$

implying the $a(W, L)$ -fold degeneracy of the states with the energy $\varepsilon = \pm t$, where

$$a(1, L) = 2, 1, 2, 1, 2, 1, 2, 1, \dots, \quad (3a)$$

$$a(2, L) = 1, 1, 0, 2, 0, 1, 1, 0, 2, 0, \dots, \quad (3b)$$

$$a(3, L) = 2, 0, 2, 0, 2, 0, 2, 0, 2, 0, \dots, \quad (3c)$$

$$a(4, L) = 1, 2, 0, 3, 0, 2, 1, 1, 2, 0, \dots. \quad (3d)$$

We have displayed the full spectrum for some examples in Fig.2.

One of our main results is that there are no zero-energy states in finite-length nanoribbons, though infinite-length nanoribbons have the flat band consisting of degenerated zero-energy states^{1,2}.

There are two interesting features in the energy spectra. First, the level spacings are almost equal near the Fermi energy $|\varepsilon| < t$, as shown in Fig.2. Second, the band gap decreases inversely to the length, and zero-energy states emerge as $L \rightarrow \infty$, as shown in Fig.3. This is consistent with the fact that infinite-length nanoribbons have the flat band made of degenerated zero-energy states^{1,2}. Hence, a sufficiently long nanoribbon can be regarded practically as a metal. In this energy region the energy spectrum is that of Dirac electrons⁹. Hence we expect to ascribe these features to the property of Dirac electrons, though detailed mechanisms are yet to be studied in future works.

Graphene nanodisks: We proceed to investigate the electronic properties of a wide class of nanodisks. In particular, we are interested whether there exist nanodisks which have zero-energy states. The basic element of graphene nanodisks is a benzene. Every nanodisk can be constructed by connecting several benzenes. There are a large variety of graphene nanodisks, where typical examples are displayed in Fig.4. We have studied hexagonal, parallelogrammic and trigonal nanodisks with zigzag or armchair edges.

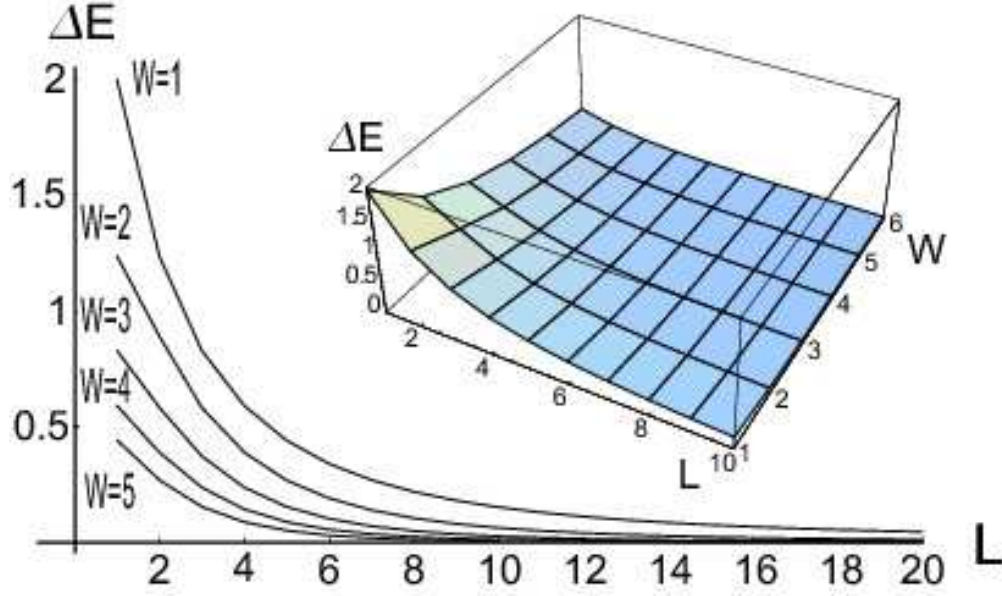


FIG. 3: (Color online) Band gap of zigzag nanoribbons with length L . The horizontal axes is the length L and the vertical axes is the energy gap ΔE in units of $t = 3\text{eV}$. Inset: 3D plot of band gap as a function of L and W .

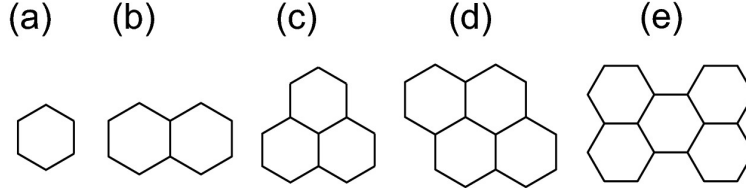


FIG. 4: Geometric configurations of typical graphene nanodisks. (a) Benzene. (b) Naphthalene. (c) Trigonal zigzag nanodisk (phenalene). (d) Pyrene. (e) Perylene.

Diagonalizing the Hamiltonian (1) explicitly, we have explicitly constructed the energy spectrum for each of nanodisks. We have displayed the density of states for several nanodisks with trigonal zigzag shape in Fig.5(a) and parallelogrammic zigzag shape in Fig.5(b). We have checked that there exist zero-energy states only in trigonal zigzag nanodisks. The emergence of zero-energy states in graphene nanodisks is very rare.

Trigonal zigzag nanodisks are prominent in their electronic properties because there exist zero-energy states. We have found that the determinant associated with the Hamiltonian

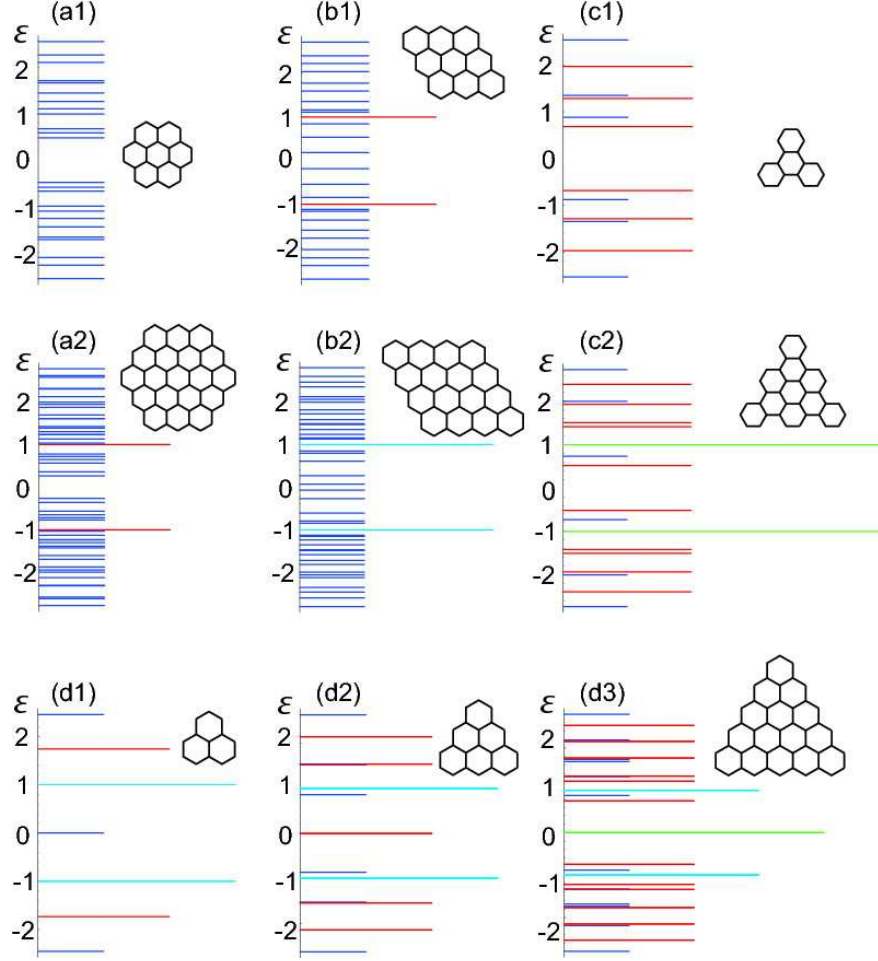


FIG. 5: (Color online) Density of states for typical zigzag nanodisks, The horizontal axis is degeneracy and the vertical axis is the energy ε in units of $t = 3\text{eV}$. (a) Hexagonal zigzag nanodisks. (b) Parallelogrammic zigzag nanodisks. (c) Trigonal armchair nanodisks. (d) Trigonal zigzag nanodisks. There are degenerated zero-energy states in all trigonal nanodisks, and they are metallic. There are no zero-energy states in all other nanodisks, and they are semiconducting.

(1) has a factor such that

$$\det [\varepsilon I - H(N_C)] \propto \varepsilon^N (\varepsilon - t)^{a(N)} (\varepsilon + t)^{a(N)}, \quad (4)$$

implying the N -fold degeneracy of the zero-energy states and the $a(N)$ -fold degeneracy of the states with the energy $\varepsilon = \pm t$, where

$$a(N) = 3, 3, 3, 3, 3, 5, 3, 5, 3, 7, 3, 7, 3, \dots, \quad (5)$$

for $N = 1, 2, 3, \dots$. Here, $N + 1$ is the number of benzenes in one of the edge of the trigonal

nanodisk, which is related to the number of carbons by $N_C = N^2 + 6N + 6$. It is remarkable that we can engineer nanodisks equipped with an arbitrary number of degenerate zero-energy states.

Discussions: Graphene nanodisks may be regarded as quantum dots made by graphene. Finite-length graphene nanoribbons and graphene nanodisks would be basic components of graphene nanocircuits.

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